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Patentanmeldung Nr.

Patent application No. Demande de brevet n°

02292767.7

Der Präsident des Europäischen Patentamts; Im Auftrag

For the President of the European Patent Office Le Président de l'Office européen des brevets D.O.

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Red-coloured electric lamp

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Red-coloured electric lamp.

FIELD OF THE INVENTION

The present invention relates to electric lamps. In particular the invention relates to an electric lamp having a glass envelope, the glass being red coloured.

The invention applies to incandescent lamps and more particularly to automotive signal lamps, e.g. indicator lamps.

BACKGROUND OF THE INVENTION

Automotive signal lamps must have specific colours defined by international traffic regulations. For example, automotive signalling functions like tall, stop or fog lighting require red lamps. In order to obtain the red colour as defined by international traffic regulations, the lamps in prior-art are usually coated with a red varnish or lacquer. A disadvantage of the prior-art lamps is that the lacquer or varnish may degrade and may eventually peel off from the wall of the lamp envelope. Actually, these red coatings usually consist of vulnerable constituents that have a relative low thermal resistance. Another disadvantage of the prior-art lamps is that additional steps are necessary during the manufacturing process of the lamp for cleaning and varnishing the lamp envelope. The manufacturing cost is increased by these additional steps.

25 SUMMARY OF THE INVENTION

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It is an object of the invention to provide an electric lamp suitable for automotive applications, said lamp having a glass envelope, the glass being red coloured.

According to the invention, these objects are achieved by an electric lamp as mentioned in the opening paragraph, the glass composition comprising copper between 0.1 and 2% by weight, tin between 0.1 and 2% by weight, barium between 7 and 11% by weight and strontium between 1 and 5% by weight.

No additional manufacturing step is necessary during the production of an electric lamp according to the invention, since the specific colour point of the glass envelope is realized by the particular composition of the glass. At least, the steps of cleaning and varnishing are suppressed. Due to its specific composition, the glass may have a red colour point sultable for automotive signal lamps, as defined by international traffic regulations.

Moreover, the coloured glass obtained in accordance with this glass

composition yields to a better quality glass, since the obtained red colour due to the glass composition stays forever, which may not be the case of varnished glasses. Actually, the use of barium and strontium lowers the ion-conductivity of the glass, which results in a thermo stable colour of the glass at lamp operating temperatures.

Furthermore, such a glass is particularly suitable for automotive signal lamps, because the presence of barium increases the electric resistivity of the glass, which is required for the electrical feed-through.

In an advantageous embodiment, the glass composition comprises the following constituents, expressed in percentages by weight:

SiO ₂	60-72
Al ₂ O ₃	1-5
Li ₂ O	0.5-1.5
Na ₂ O	5-9
K₂O	3-7
MgO	1-2
CaO	1-3
SrO	1-5
ВаО	7-11
CuO	0.1-2
SnO₂	0.1-2

The SiO_2 content is ilmited to 60-72%. These contents, in combination with the other constituents, leads to a readily meltable glass. Al_2O_3 improves the chemical resistance and the corrosion resistance of the glass. The alkaline metal oxides Li_2O , Na_2O and K_2O are used as melting agent and reduce the viscosity of the glass. MgO and CaO reduce the liquefying temperature and the melting temperature of the glass. Such a glass is lead-free, cadmium-free and selenium-free, which elements are harmful for the environment.

The invention and additional features, which may be optionally used to implement the invention, are apparent from and will be elucidated with reference to the drawings described hereinafter.

BRIEF DESCRIPTION OF THE DRAWINGS

The invention will now be described in more details, by way of example, with reference to the accompanying drawings, in which:

 Fig. 1 shows a schematic chart illustrating an example of an electric lamp according to the invention.

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- Fig. 2 shows a chromaticity diagram showing the characteristics in the colour triangle of red coloured glasses according to the invention.

DETAILED DESCRIPTION OF THE INVENTION

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Figure 1 shows an electric automotive signal lamp 1 also called indicator lamp comprising:

- a lamp envelope or bulb 2 made out of red coloured glass, having a wall thickness comprised between, for example, 0.3 mm and 1.1 mm,
- a mount 3, comprising two lead wires 3a and 3b hold by a bead 4
 mounted inside the glass bulb 2 for supporting a coiled filament 5,
- an exhaust tube 7, heated and sealed up with the mount 3 and the bulb 2, thereby forming a vacuum-tight pinch for exhausting gasses from the lamp envelope 2 and for introducing inert gas into the lamp envelope during the manufacturing process of the lamp,
- an electric contact 8 connected to the mount 3 for the lamp to be
 electrically supplied by the electric circuits of the car,
 - a metal cap 9 to fit in a holder of the lamp set.

In an advantageous embodiment of the invention, the starting materials for making the glass are quartz sand, spodumene, dolomite, the carbonates of LI, Na, K, Sr and Ba, CuO and SnO₂.

An electric lamp in accordance with an advantageous embodiment of the invention, has a glass bulb with a glass composition comprising the constituents as listed in Table 1.

Constituent	Composition
	(% by weight)
SIO ₂	60-72
Al ₂ O ₃	1-5
Li ₂ O	0.5-1.5
Na₂O	5-9
K₂O	. 3-7
. MgO	1-2
CaO	1-3
SrO	1-5
ВаО	7-11
CuO	0.1-2
SnO₂	0.1-2

Table 1: glass composition according to an advantageous embodiment of the invention.

In this table, the percentages by weight of the oxidic forms of the constituents are given. This does not necessary implies that these elements are present in the glass under this oxidic form. For example, copper in the glass might be present as metallic Cu, Cu $^+$, CuO or other forms of copper. As a consequence, expressions like "the glass composition comprises element X between α and $\beta\%$ by weight" mean that all the forms of element X comprised in the glass composition represent between α and $\beta\%$ by weight.

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SiO₂ serves as a network former in the glass. The SiO₂ content is limited to 60-72% by weight, leading in combination with the other constituents to a readily meltable glass. If the content is below 60% by weight, the cohesion of the glass and the chemical resistance are reduced. If the content is above 72% by weight, the glass formation is impeded and the risk of surface crystallization increases. Al₂O₃ improves the chemical resistance and the corrosion resistance of the glass. Below 1% by weight the effect is too small and the crystallization tendency of the glass increases. Above 5% by weight the viscocity and the softening temperature of the glass increase too much, which affects the workability of the glass. The alkaline metal oxides Li₂O, Na₂O and K₂O are used as melting agent and reduce the viscosity of the glass. They increase the electric resistance of the glass (mixed-alkali effect). BaO has the favorable property that it increases the electric resistance of the glass and reduces the softening temperature of the glass. Below 7% by weight, the melting temperature, the softening temperature and the working temperature increase too much. Above 11% by weight, the liquidus temperature and hence the crystallization tendency increase too much. The alkaline-earth metaloxides SrO, MgO and CaO have the favorable property that they reduce the liquefying temperature and the melting temperature of the glass.

The glass may additionally contain some Fe_2O_3 as an impurity originating from the raw materials used. Also TiO_2 , ZrO_2 and MnO can be found as trace elements.

The red colour of the glass according to the invention is obtained by adding between 0.1 and 2% by weight of CuO and a reducing agent, e.g. carbone or charcoal, in the glass composition. SnO₂ is also added in the glass composition.

In the presence of a reducing agent and SnO₂, copper colours silicate glasses red which is explained by the possible precipitation of Cu in metallic form, as it will be described hereinafter.

An electric lamp in accordance with another embodiment of the invention, has a glass bulb with a glass composition comprising the constituents as listed in Table 2.

Constituent	Composition
	(% by weight)
SiO ₂	60-72
Al ₂ O ₃	1-5
Li ₂ O	0.5-1.5
Na₂O	5-9
K₂O	3-7
MgO	1-2
CaO	1-3
SrO	1-5
BaO	7-11
CuO	0.6-0.9
SnO ₂	0.3-1.8
Fe ₂ O ₃	0 - 0.05

Table 2: glass composition according to another embodiment of the invention.

With respect to the element whose weight percentage has a lower limit equal to zero, it means that the element may not be added as raw material but yet be present in the ready glass as a result of contamination of the raw materials.

The glasses made with the constituents as listed in Table 1 or 2 have characteristics as shown in Table 3.

Physical property	Value
T _{strain} (low stress relief temperature)	455°C
T _{anneal} (high stress relief temperature)	490°C
T _{soft} (softening temperature)	675°C
T _{meit} (melting temperature)	1490°C
Specific mass	2.62*10 ³ kg.m ³
Specific resistance	7.9*10 ⁶ Ω.m
Linear expansion coefficient (25-300°C)	9.1*10 ⁻⁶ /°C

Table 3: Physical properties of the glass according to the invention.

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The glass making process is described hereinafter. A batch is prepared by weighing and mixing all oxidic components mentioned above. The batch is fed to a conventional continuous melting tank. Adjustments of the recipe can be made by adding separate ingredients in the feeding system for enhancing the colourization. The melting conditions, including temperature and gas atmosphere, are adjusted to obtain a stable processing for melting, refining and colour stabilization.

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In series of complex reactions, the excesses gasses, including CO, are removed from the glass melt to avoid airline in the formed tubes. Glass tubes are made at the end of the glass manufacturing process using the well-known Danner process in the factory. However, the well-known Vello process could also be applied. Part of the tube is heated to make lamp bulbs.

The striking of the glass might be explained by the presence of metallic Cu in crystals of colloidal size, in equilibrium with Cu⁺. Furthermore, it appears that striking requires a certain degree of nucleation, which is why SnO₂ is added. Cu is introduced in the form of the oxide in combination with a reducing agent. In this example, the reducing agent is carbon, but any other reducing agent could be used including Al and Si. Suitable time and temperature of striking, which depend on the basic composition, are best determined in a gradient furnace. For example, a striking temperature between 500 and 550°C might be used. The time of striking might be between 0.5 and 3 hours.

Copper is introduced as CuO in a percentage comprised between 0.1 and 2 % by weight. Larger amounts of copper are harmful, as they decrease transmissivity in the red region. Lower concentrations do not produce colouring. Under reducing conditions, an equilibrium is obtained between Cu^{2+} , Cu^{+} and Cu. When sufficient Cu^{+} ions are present in the glass, the concentration of Cu in equilibrium with Cu^{+} exceeds the solubility limits and Cu is precipitated. The red colour is obtained by colloidally dispersed Cu particules in equilibrium with Cu^{+} , when the bivalent copper has disappeared. The reducing element should therefore be able to reduce all Cu^{2+} . In this example, the reducing element C is chosen in a proportion C/Cu = 1.67.

The function of tin might be that of a metallophilic element. As soon as a nucleus of a Cu crystal has formed, it selectively attracts the Sn²⁺ ions, which form an efficient barrier against further growth of the metal crystal and thus stabilises the colloidal dispersion of the Cu and prevent further growth of the Cu atom aggregates and their overstriking.

Figure 2 shows a variety of colour points of red coloured glass for use in the glass envelope of signal lamps according to international traffic regulations,

with respect to X and Y co-ordinates in the chromaticity chart. This colour point may be achieved with the glass composition in accordance with the invention described above. It is noted that the exact composition of the glass which gives the colour point depends on the production of the glass, particularly the reducing state, and on the curing after bulb blowing.

In Europe, a red colour point for automotive indicator lamps is defined by the ECE regulation, known to the person skilled in the art. It corresponds to the area shown in continuous lines of Figure 2. The red ECE-region is determined by the following colour coordinates: (0.657, 0.335); (0.665, 0.335); (0.732, 0.27); (0.728, 0.27).

The SAE (Society of Automotive Engineers) has proposed another region, which is determined by the following colour coordinates: (0.65, 0.33); (0.67, 0.33); (0.7367, 0.2653); (0.7164, 0.2636). This region is represented in dotted lines on Figure 2.

The GTB (Groupe de Travail de Bruxelles) commission has proposed a new larger area, which encloses both current ECE and SAE colour boundaries. This is known as the CIE-region.

The triangles in the chart of Fig.2 show the colour points obtained with a glass of 0.5 mm thickness comprising 0.9% by weight of copper, 0.6% by weight of tin, 9.0% by weight of barium and 3.0% by weight of strontium. The striking temperature is 540°C. The results are given for striking times of 2 and 3 hours.

The drawings and their description hereinbefore illustrate rather than limit the invention. It will be evident that there are numerous alternatives which fall within the scope of the appended claims. In this respect, the following closing remark is made.

The word "comprising" does not exclude the presence of other elements than those listed in a claim. The word "a" or "an" preceding an element does not exclude the presence of a plurality of such elements.

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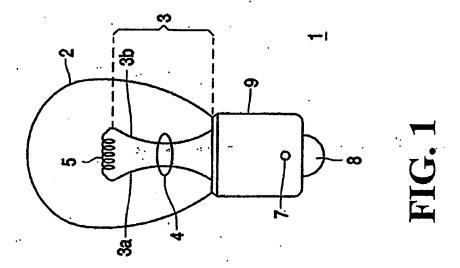
<u>Claims</u>

- 1. An electric lamp having a glass envelope, the glass being red coloured, the glass composition comprising copper between 0.1 and 2% by weight, tin between 0.1 and 2% by weight, barium between 7 and 11% by weight and strontium between 1 and 5% by weight.
- 2. An electric lamp as claimed in claim 1, wherein the glass composition, expressed in percent by weight of the oxidic forms of the constituents, comprises:

SIO₂	60-72
Al ₂ O ₃	1-5
Li ₂ O	0.5-1.5
Na₂O	5-9
K₂O	3-7
MgO	1-2
CaO	1-3
SrO	1-5
BaO	7-11
CuO	0.1-2
SnO ₂	0.1-2

Abstract

The invention relates to electric lamps and more particularly to automotive signal lamps. A glass composition is described for use in electric lamps, which glass is red coloured. The glass composition comprises copper between 0.1 and 2% by weight, tin between 0.1 and 2% by weight, barium between 7 and 11% by weight and strontium between 1 and 5% by weight.



Y-value ♠

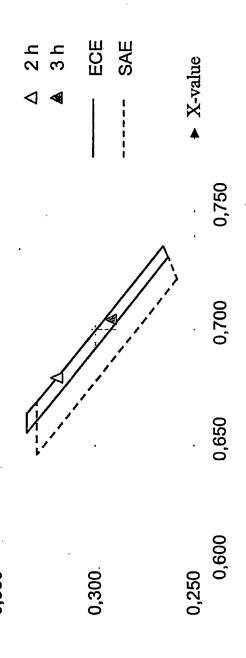


FIG. 2